Magnetic and Mössbauer studies on rare-earth-containing Heusler alloys Pd_2RSn (R = Tb—Yb)

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Magnetic susceptibility and ^{119}Sn Mössbauer studies have been carried out on a new series of rare-earth-containing Heusler alloys having the formula Pd_2RSn (R = Tb—Yb). The Tm and Yb compounds in this series along with Lu, Sc, and Y compounds are superconducting. The magnetic susceptibility of Pd_2TmSn and Pd_2YbSn deviates from the Curie-Weiss behavior at low temperatures indicating that crystalline electric field effects are appreciable. Analysis of the magnetic susceptibility data in terms of crystalline electric fields shows that the ground state of the Tm^{3+} ion is nonmagnetic which, therefore, does not affect the superconducting state. The susceptibility of Yb^{3+} ions at low temperatures is also reduced from the free-ion value due to the crystalline electric field interaction. The Tb- and Dy-containing compounds order antiferromagnetically with Néel temperatures of 9 and 15 K, respectively, while Er- and Ho-containing compounds are paramagnetic down to 1.4 K. The hyperfine field at the Sn site in Pd_2TbSn is about 50 kOe but is only about 10 kOe in Pd_2DySn at 4.2 K.

I. INTRODUCTION

Heusler alloys are intermetallic compounds having the general formula X_2YZ. In the traditional Heusler alloys, X is generally one of the d transition elements such as Cu, Co, Ni, Pd, etc. Y is another d element e.g., Mn, Co; and Z is an sp element such as Al, In, Sn, etc.[1] These alloys have the cubic $L2_1$ structure and have been extensively studied for their magnetic properties. Recently, alloys of the Heusler composition have been synthesized which contain rare earths (R) as one of the constituent elements. These include Pd_2RSn,[2] Ag_2RIn,[3] Au_2YIn,[4] etc. The Pd_2RSn compounds form only for heavier rare earths starting from Tb up to Lu (and for Sc and Y), possibly because of the respective sizes of the rare-earth atoms.

In the Pd_2RSn series, the lattice parameters indicate that the rare-earth ions are in a trivalent state. It is interesting to note that, in this series, the compounds with R = Tm, Yb, Lu, Y, and Sc exhibit superconductivity. In these compounds the distance between rare-earth atoms is about 4.7 Å which is much smaller than the corresponding distance of 6.5 Å in the well-known superconducting RMo_6S_8 compounds.[5] Moreover, the exchange interaction between the rare-earth spins and the conduction-electron spins is estimated[2] to be about 5 times larger in Pd_2RSn (obtained from suppression of T_c in the presence of magnetic rare-earth impurities in Pd_2YSn) than that in RMo_6S_8 compounds. Therefore, it is somewhat striking that the compounds Pd_2TmSn and Pd_2YbSn are superconducting in spite of these adverse conditions. In order to understand the magnetism of rare-earth ions in the superconducting Pd_2RSn compounds, we have carried out magnetic susceptibility and ^{119}Sn Mössbauer measurements on these compounds. We find that due to the presence of crystalline electric fields, the degeneracy of the ground J multiplet of Tm^{3+} is lifted, resulting in a nonmagnetic ground state at low temperatures which does not lead to appreciable pair breaking and hence does not suppress superconductivity. The susceptibility of Yb^{3+} ions is also considerably reduced from the free-ion value due to lifting of the degeneracy of the ground J manifold by crystalline electric fields (CEF). This coupled with the fact that the Landé g factor for Yb^{3+} is small considerably reduces the pair-breaking effect due to Yb^{3+} ions, enabling the superconducting state to persist. However, Yb^{3+}, being a Kramer's ion, cannot have zero magnetic moment, and this leads[2,6] to magnetic ordering and to the coexistence of superconductivity and antiferromagnetic order in this compound at still lower temperatures. Magnetic susceptibility and ^{119}Sn Mössbauer measurements on the nonsuperconducting members of Pd_2RSn series are also presented.

II. EXPERIMENTAL

The Pd_2RSn (R = Tb—Yb) alloys were prepared by arc melting of the stoichiometric amounts of the constituent elements in a purified argon-gas atmosphere. The alloy ingots were turned over and repeatedly melted to obtain homogeneous samples. The ingots were wrapped in tantalum foils, sealed in vacuum and annealed at 800 °C for 7d. Powder x-ray diffraction patterns were obtained using Cu K_α radiation on a Rigaku diffractometer equipped with a monochromator. Susceptibility measurements were carried out in the temperature range 5—300 K using a SQUID (superconducting quantum interference device) magnetometer. The superconducting and magnetic ordering temperatures were determined by the use of an ac bridge technique. ^{119}Sn Mössbauer measurements were carried out at various temperatures using a conventional transmission Mössbauer spectrometer with a $CaSnO_3$ source held at room temperature. The absorbers of Heusler compounds were cooled down to 1.5 K in a liquid-helium cryostat.

TABLE I. Lattice parameter a, effective paramagnetic moment μ_{eff}, paramagnetic Curie temperature Θ_P, antiferromagnetic ordering temperature T_N, and superconducting transition temperature T_c of the Heusler alloys Pd_2RSn.

Compound	a (Å)	μ_{eff} (Expt.) (μ_B)	μ_{eff} (free ion) (μ_B)	Θ_P (K)	T_N (K)	T_c (K)
Pd_2ScSn	6.503					2.15
Pd_2YSn	6.716					4.55
Pd_2TbSn	6.740	9.95	9.72	−8.6	9.0	
Pd_2DySn	6.722	10.83	10.85	−9.3	15.0	
Pd_2HoSn	6.705	10.67	10.61	−6.2	a	
Pd_2ErSn	6.692	9.59	9.58	−7.6	a	
Pd_2TmSn	6.670	7.4	7.56	0		2.82
Pd_2YbSn	6.658	4.34	4.54	−4.3	0.23[b]	2.42
Pd_2LuSn	6.645					3.05

[a]Not ordered magnetically down to 1.4 K (see text).
[b]Exhibits coexistence of superconductivity and antiferromagnetism.

III. RESULTS AND DISCUSSION

Room-temperature powder x-ray diffraction studies showed that all the Pd_2RSn (R=Tb–Yb) compounds were single-phase materials having the cubic $L2_1$ structure, which is shown in Fig. 1. The lattice constants determined by the least-squares fit of observed d values are given in Table I. The results of magnetic susceptibility (both ac and dc) and ^{119}Sn Mössbauer measurements for each of the compounds are discussed below and also summarized in Table I.

A. Pd_2TmSn

ac susceptibility measurements showed that this compound becomes superconducting with a transition temperature of 2.82 K. The dc magnetization at 5 K is observed to vary linearly with the applied field consistent with the paramagnetic nature of the compound. Therefore, the temperature dependence of magnetization was investigated in a fixed field of 5 kOe. Figure 2 shows the plot of inverse molar susceptibility versus temperature for Pd_2TmSn. Above about 50 K the susceptibility follows a Curie-type (C/T) behavior, where C is the Curie constant, with an effective paramagnetic moment $\mu_{\text{eff}}=7.4\mu_B$ which is close to the value for the free ion. However, below about 50 K, deviation from the Curie-type behavior is observed, although it is not very pronounced. The deviation is seen more clearly by plotting effective moment $\mu_{\text{eff}}=(3kT\chi_M/N\mu_B^2)^{1/2}$ versus temperature. If χ_M varies as C/T, then $\mu_{\text{eff}}(T)$ should be independent of temperature. However, the observed $\mu_{\text{eff}}(T)$ deviates from a constant value at low temperatures. The deviation from the Curie-type behavior is ascribed to CEF effects.

In the Heusler $L2_1$ cubic structure of Pd_2RSn alloys, the R ion occupies a site of local cubic symmetry. Thus, it is subject to a cubic CEF, the Hamiltonian for which can be written as

$$\mathcal{H}=B_4^0(O_4^0+5O_4^4)+B_6^0(O_6^0-21O_6^4)\,, \tag{1}$$

where O_n^m are the Steven's operators in terms of the angular-momentum operators and are given in Ref. 7. B_4^0 and B_6^0 are, respectively, the strength of fourth- and sixth-degree terms in the CEF Hamiltonian. It is con-

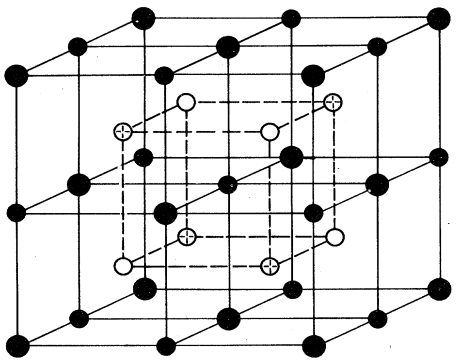

FIG. 1. The Heusler $L2_1$ structure.

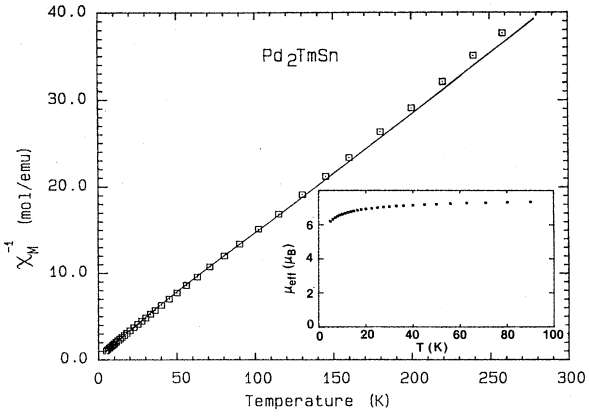

FIG. 2. χ_M^{-1} vs temperature (T) and μ_{eff} vs T for Pd_2TmSn. The solid line is the fit based on CEF calculations. The parameters used are $W=1.59$ K and $x=-0.61$.

venient to write the CEF Hamiltonian in the notation of Lea, Leask, and Wolf (LLW) (Ref. 7) as

$$\mathcal{H}_{\rm CEF}=W[\,x(O_4^0+5O_4^4)/F(4) +(1-|x|)(O_6^0-21O_6^4)/F(6)]\,, \quad (2)$$

where W and x are given by

$$Wx=B_4^0F(4) \quad (3)$$

and

$$W(1-|x|)=B_6^0F(6) \quad (4)$$

in which $F(4)$ and $F(6)$ are certain numerical factors and are given by LLW for all rare-earth ions. In Eq. (2), W acts like a scale factor and x ($-1.0\le x\le 1.0$) measures the ratio of fourth- to sixth-degree terms in the CEF Hamiltonian. CEF interaction lifts the degeneracy of ground J manifold of the Hund's state and in the case of Tm^{3+} ($4f^{12}$, $^3H_6$) (non-Kramers ion) gives rise to the levels Γ_1, Γ_2 (singlets), Γ_3 (doublet), Γ_4, $\Gamma_5^{(1)}$, and $\Gamma_5^{(2)}$ (triplets). The Hamiltonian given by Eq. (2) along with the Zeeman term was diagonalized to obtain energy eigenvalues and the eigenvectors from which magnetic susceptibility was calculated. The effect of exchange interaction between rare-earth ions was included in the molecular-field approximation by writing the susceptibility as[8]

$$\chi_{\rm obs}^{-1}=\chi_{\rm CEF}^{-1}-\lambda_M\,, \quad (5)$$

where $\chi_{\rm obs}$ is the observed susceptibility and $\chi_{\rm CEF}$ is the susceptibility in the presence of CEF interactions. The observed susceptibility was fitted to obtain the values of W and x, and in turn the CEF level scheme. The molecular-field constant λ_M for Pd_2TmSn was taken as zero. The best fit to the susceptibility is obtained for positive values of W (in the range of 0.5 to 1.6 K depending on x) and for negative values of x ranging from $x=-0.4$ to -0.8. Fit is also obtained for some negative values of W and $x>0.8$ but this set of W and x is not consistent with the values in Pd_2YbSn (discussed below). Both these combinations yield either a Γ_3 (doublet) as the ground state with $\Gamma_5^{(1)}$ or $\Gamma_5^{(2)}$ triplet as the first excited state or vice versa. The energy separation between the ground and the first excited state is only about 10 K. For W and x values mentioned above, one is in a region of LLW diagram where Γ_3 and $\Gamma_5^{(1)}$ or $\Gamma_5^{(2)}$ are crossing. There is corroborative evidence from ^{169}Tm Mössbauer spectroscopy that the assignment of Γ_3 as ground state is correct.[9] The expectation value of J_z in each component of the doublet ground state is zero and hence the ground state is nonmagnetic. The $\Gamma_5^{(1)}$ and $\Gamma_5^{(2)}$ triplets, however, have a nonzero moment.

The rare-earth spins tends to break the Cooper pairs due to exchange interaction with the conduction-electron spin. This interaction is given by the Hamiltonian

$$\mathcal{H}=-2J_{sf}\mathbf{S}\cdot\mathbf{s}\,. \quad (6)$$

For most of the rare earths one may take the projection of $\mathbf{S}$ onto $\mathbf{J}$ and write the above Hamiltonian as $2J_{sf}(g_J-1)\,\mathbf{J}\cdot\mathbf{s}$ where $\mathbf{S}$ is the spin of the rare-earth ion $\mathbf{J}$ its total angular momentum, g_J is the Landé g factor, and J_{sf} is the exchange constant for interaction between rare-earth (or the $4f$-electron) spins $\mathbf{S}$ and conduction-electron spins $\mathbf{s}$. The theory of pair breaking by magnetic impurities has been worked out[10] by Abrikosov and Gor'kov and by Fulde and Maki. The pair-breaking parameter involves g_J-1 and the thermal average of J_z. The latter is zero for the Γ_3 ground state of Tm^{3+} with a contribution coming only from the excited state. Therefore, the superconducting state is not influenced by Tm^{3+} ions in Pd_2TmSn.

B. Pd_2YbSn

The Pd_2YbSn compound studied by us was found to be superconducting with T_c of 2.42 K. Figure 3 shows the plot of inverse susceptibility versus temperature and the inset shows the variation of $\mu_{\rm eff}$ versus temperature. A somewhat more pronounced deviation from the Curie-Weiss behavior than that in Pd_2TmSn is observed at low temperatures which is attributed to the CEF effects. The susceptibility was fitted in a manner analogous to the one used for Pd_2TmSn and the fit is shown in Fig. 3. The fit is obtained for a range of values of W and x which are consistent in sign with those in Pd_2TmSn. One such fit is shown in Fig. 3. The Yb^{3+} ($4f^{13}$,$^2F_{7/2}$) is an odd electron system and according to Kramer's theorem the CEF will leave each state at least twofold degenerate. The resulting ground state is either a Γ_6 or a Γ_7 doublet which has a susceptibility that is reduced from the free-ion value. This reduction is by a factor of 3 for Γ_6 and by 2.34 for Γ_7. Besides, the factor g_J-1 is small for Yb^{3+}. These two factors again lead to a weak pair breaking and, therefore, superconductivity is not suppressed in this compound.

C. Pd_2HoSn and Pd_2ErSn

These compounds investigated by us are neither superconducting nor magnetically ordered down to 1.4 K. However, Ishikawa *et al.*,[2] report ordering temperatures of $\sim$2 K for Ho compound and $\sim$0.7 K for Er compound. In this respect the magnetic ordering tempera-

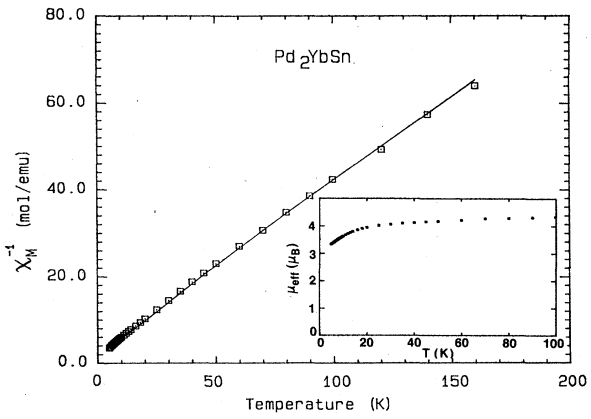

FIG. 3. χ_M^{-1} vs temperature (T) and $\mu_{\rm eff}$ vs T for Pd_2YbSn. The solid line is the fit based on CEF calculations. The parameters used are $W=-11.9$ K, $x=-0.65$, and $\lambda_M=-0.33$ mol/emu.

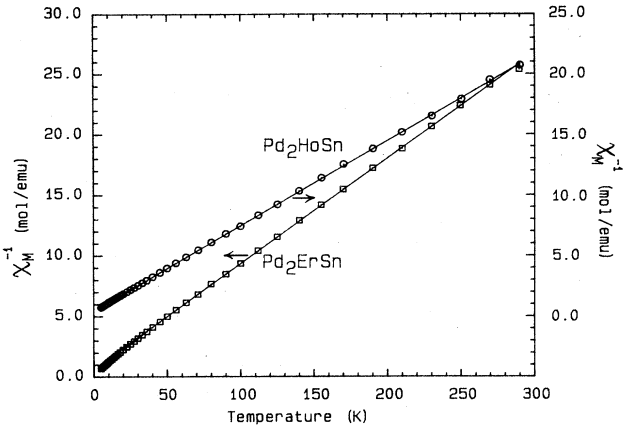

FIG. 4. χ_M^{-1} vs temperature for Pd_2HoSn and Pd_2ErSn.

tures of Pd_2RSn compounds do not follow the de Gennes rule.[11] The magnetic susceptibilities of Pd_2HoSn and Pd_2ErSn are independent of the applied field and follow Curie-Weiss behavior with some deviations at very low temperatures (Fig. 4). Again, the deviations are presumably due to CEF effects. The effective paramagnetic moments (obtained from susceptibility data above 50 K) are close to the free-ion values for the corresponding trivalent rare-earth ions. The susceptibility has not been analyzed in terms of CEF splitting. ^{119}Sn Mössbauer measurements show a single line throughout the temperature range of 1.4 to 300 K in both these compounds.

D. Pd_2TbSn and Pd_2DySn

ac susceptibility measurements indicate that these compounds are magnetically ordered at low temperature. This is also borne out by the dc magnetic susceptibility measurements (Figs. 5 and 6) in 5 kOe applied field. A peak in the susceptibility is observed at 9 K in Pd_2TbSn and at 15 K in Pd_2DySn indicative of the antiferromagnetic ordering of the rare-earth sublattice in these compounds. In the paramagnetic state the susceptibilities of both these compounds follow Curie-Weiss behavior with effective

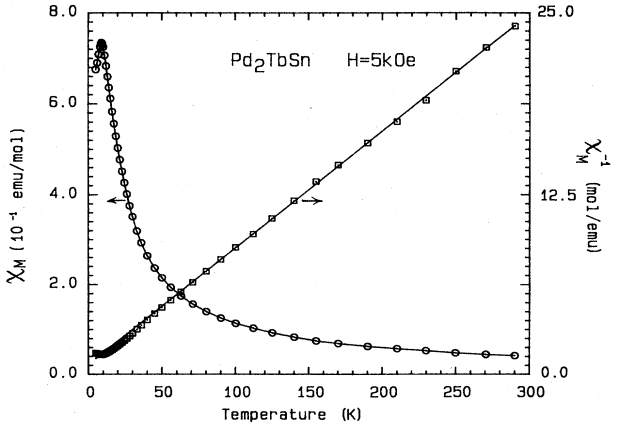

FIG. 5. χ_M versus temperature and χ_M^{-1} versus temperature for Pd_2TbSn. The solid line is the Curie-Weiss fit $\chi_M = C/(T-\Theta_P)$.

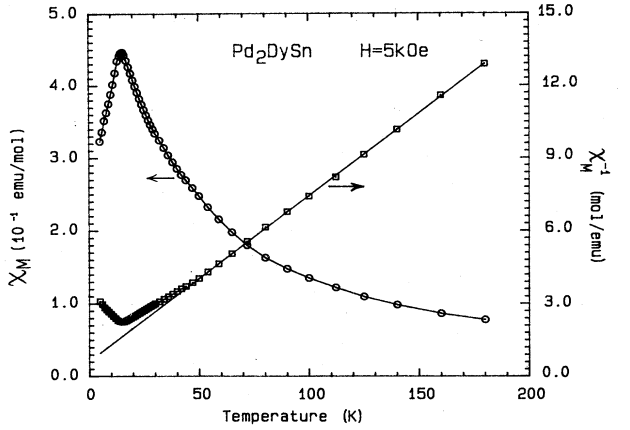

FIG. 6. χ_M versus temperature and χ_M^{-1} versus temperature for Pd_2DySn. The solid line is the Curie-Weiss fit $\chi_M = C/(T-\Theta_P)$.

paramagnetic moments close to those of the respective free trivalent rare-earth ions.

It should be mentioned that both these compounds undergo a low-temperature crystallographic transformation to a low symmetry phase.[12] Hence, the CEF experienced by the rare earth (Tb and Dy) will have a major axial term (B_2^0). This can indeed generate the nearly-free-ion moment in the ground state depending on the sign of the B_2^0 term.

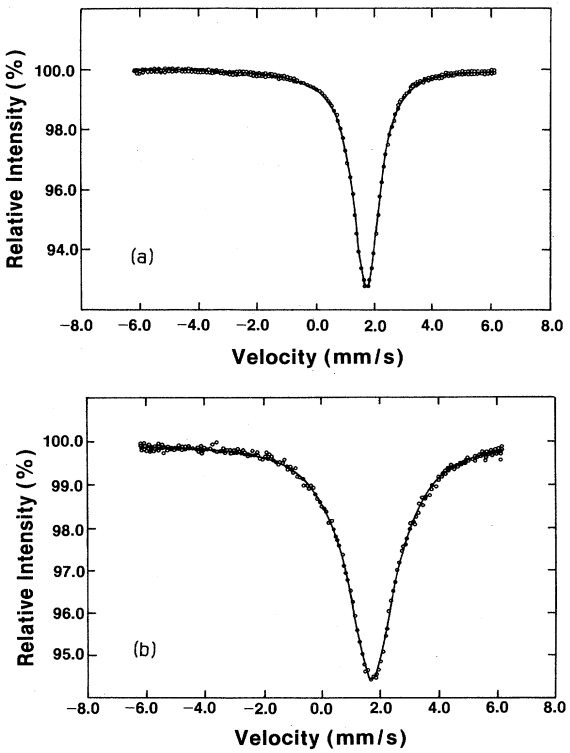

FIG. 7. ^{119}Sn Mössbauer spectra of Pd_2TbSn at (a) 77 K and (b) 4.2 K.

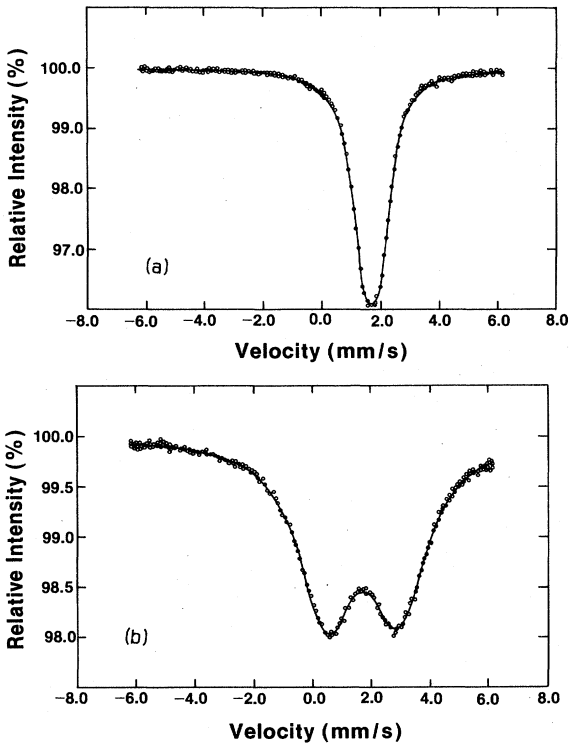

FIG. 8. ^{119}Sn Mössbauer spectra of Pd_2DySn at (a) 77 K and (b) 1.5 K.

^{119}Sn Mössbauer measurements yield a single line in both compounds at 300 K and at 77 K with a width of 0.95 mm/sec. On lowering the temperature below the Néel temperature, the ^{119}Sn Mössbauer in Pd_2TbSn gives rise to a hyperfine split pattern from which the field at the Sn site is estimated to be about 50 kOe. However, in Pd_2DySn, only line broadening in the Mössbauer patterns is observed in the magnetically ordered state (see Figs. 7 and 8). Thus, the transferred hyperfine field at the Sn site in Pd_2DySn is small and is estimated to be about 10 kOe. The difference in the field at the Sn site in Tb and Dy compounds may be because of the different types of antiferromagnetic ordering of the rare-earth moments in the two compounds. Neutron-diffraction measurements are needed to obtain the magnetic structure in the ordered state.

IV. CONCLUSIONS

In conclusion, magnetic and ^{119}Sn Mössbauer studies have been carried out on a new series of rare-earth containing Heusler alloys of the type Pd_2RSn (R = Tb—Yb). Some of these exhibit superconductivity while others in this series are magnetically ordered. The CEF's are found to be appreciable in the Tm and Yb compounds, which become superconducting at low temperatures. The ground state of Tm^{3+} in Pd_2TmSn is a nonmagnetic doublet Γ_3. The low-temperature susceptibility of Yb^{3+} in Pd_2YbSn is also reduced from the free-ion value and the resulting ground state is either Γ_6 or Γ_7. The Tb- and Dy-containing compounds order antiferromagnetically while Er- and Ho-containing compounds are paramagnets down to 1.4 K. The hyperfine field at the Sn site is very different in antiferromagnetically ordered Pd_2TbSn than that in Pd_2DySn.

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